



Unlocking the Structure and Dynamics of Thin Polymeric Films

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Final Report

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14. ABSTRACT Polymers, either by deliberate design or by virtue of their mode of synthesis, are inherently inhomogeneous. Commercial polymers may be comprised of four or more monomeric building blocks, and these chemically-distinct groups are expected to selectively partition and interact with the interfaces. The objective of this project is to understand on a molecular level how changes in the interfacial structure that are inherent in thin films affects how polymers behave. A number of technically relevant polymeric systems were chosen for study. These were model photoresist polymers similar to the commercial TER60 photoresist; statistical copolymers of methyl methacrylate and a fluorinated monomer; block copolymers of styrene and a polar charged monomer; statistical copolymers of styrene and acrylonitrile. The initial aspect examined in the study was the effect of polymerization mechanism on the monomer placement along the chain, i.e. the sequence distribution (see references 1 and 4). The second aspect examined was the partitioning of one component of a heterogeneous polymer to the air interface (paper 2). The third aspect examined was the ability of these polymers to form particular topographies under particular processing conditions, due to their surface properties (paper 3).				
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Abstract: Polymers, either by deliberate design or by virtue of their mode of synthesis, are inherently inhomogeneous. Commercial polymers may be comprised of four or more monomeric building blocks, and these chemically-distinct groups are expected to selectively partition and interact with the interfaces. The objective of this project is to understand on a molecular level how changes in the interfacial structure that are inherent in thin films affects how polymers behave. A number of technically relevant polymeric systems were chosen for study. These were model photoresist polymers similar to the commercial TER60 photoresist; statistical copolymers of methyl methacrylate and a fluorinated monomer; block copolymers of styrene and a polar charged monomer; statistical copolymers of styrene and acrylonitrile. The initial aspect examined in the study was the effect of polymerization mechanism on the monomer placement along the chain, i.e. the sequence distribution (see references 1 and 4). The second aspect examined was the partitioning of one component of a heterogeneous polymer to the air interface (paper 2). The third aspect examined was the ability of these polymers to form particular topographies under particular processing conditions, due to their surface properties (paper 3).

Introduction:

Thin films of polymers are ubiquitous and important. They are present as surface coatings and paints, adhesives, and in more advanced technologies such as functional microfluidic devices, batteries, displays and in the manufacture of integrated circuits. A dominating feature of thin films of polymeric substances is that their properties depend to a large extent on the interaction of their various components with interfaces. These are interfaces with air and an underlying material, perhaps a silicon wafer or a functional organic layer. The properties of polymeric films can change dramatically as the dimensions of the film decreases below several tens of nanometers, where the properties which impart their behavior in the bulk state become “diluted”, and where powerful interfacial effects become dominant. It is the objective of this project to understand on a molecular level how changes in the interfacial structure that are inherent in thin films affects how polymers behave.

It is important to understand that polymers even in their purest form are heterogeneous. This distinction with small molecules is important and has been exploited in a positive sense in many

ways. Polymers possess chain ends with enhanced librational freedom, branched structures, and in the case of copolymers, monomers of (potentially) differing surface energy along the chain. Importantly for this project the monomers can be distributed inhomogeneously within and amongst the chains. Finally, polymers have a disperse molar mass distribution, so that even samples of the narrowest molar mass dispersity still possess a distribution of chain lengths. These various components of even the simplest polymer, let alone a complex commercial polymer, will be distributed within the thin polymer film as a function of the free energy of the interfaces and the chemistry and mobility of the respective species. Understanding such processes is of immense theoretical and technological interest; with recent advances in polymerization and characterization techniques, questions of how polymer structure affects the spatial arrangement of chains and their properties can be addressed. It is the objective of this project to examine how heterogeneous chain structure, i.e. sequence distribution, can affect the spatial arrangement of components at the polymer/air interface in thin films.

The key aims to be addressed as initially stated in the project application are:

- 1) Understand how does polymer structure affects the spatial arrangement of polymer-bound entities in thin films?
- 2) Understand how this in turn affects the dynamic properties of the polymer chains?
- 3) Understand how this is important for several key application areas?

Aim 1 has been largely completed, as described below, whilst Aims 2 and 3 continue to be pursued by PhD students Mr Ao Chen, Mr Zhen Jiang and Mr Mahbub Alam. The key application areas for Aim 3 are photolithography and antimicrobial materials.

Experiment: Experimental conditions are described in detail in references 1-3. Reference 3 is attached in submitted form (accepted 9th November 2016) as it is not available on-line.

Results and Discussion:

1) Effect of RAFT polymerization on polymer sequence distributions (papers 1 and 4)

RAFT is one of the family of powerful methods for controlled radical polymerization, along with ATRP and NMP. In controlled radical polymerization the polymer chain grows across the whole conversion range, as opposed to conventional free radical (f.r.) polymerization, in which the polymer chains are created and terminate rapidly. This leads to profound differences in chain structure when polymerizing two or more monomers. In the general case the monomer types react at different rates; they have different reactivity ratios. In conventional f.r. polymerization, chains rich in the rapidly-reacting monomer (monomer A) are formed first, and the slowly-reacting monomer (B) is overwhelmingly incorporated into chains formed near the end of the reaction. In controlled f.r. polymerization, such as RAFT polymerization, each polymer chain will have a gradient in composition. The chain will consist of monomer A at the initially-formed terminus, and will be rich in monomer B and the opposite terminus. This is important for many applications where phases separation is possible. A more fundamental question is whether the presence of the RAFT agent changes the reactivity of the monomers. There are conflicting reports in the literature. In paper 1 we found that in the polymerization of styrene, acetoxy-styrene and t-butyl acrylate, three monomers important in the lithographic industry, the reactivity ratios of the monomer pair are indeed affected by the presence of the RAFT agent. Detailed measurements of the sequence distributions showed that RAFT polymers are

significantly more homogeneous compared with the conventional polymers. This has important implications for design of process for production of lithographic polymers, or polymers at interfaces.

In contrast in paper 3 (attached), where we examined the polymerization of styrene and acrylonitrile, to form polymers used in many applications such as barrier films, the reactivity ratios were unaffected by the presence of the RAFT agent. However, we found that the polymerization follows the so-called bootstrap model, in which the growing polymer chain is preferentially solvated by one monomer over the other, thus leading to changes in the local monomer concentration. The paper is important as it demonstrates that reactivity of RAFT chain ends does not in general change with monomer type, and that choice of RAFT agent is important to avoid partitioning of monomer. This is a largely unexplored field and bridges work in fundamental polymerization chemistry and the physical chemistry of reaction mixtures.

2) Surface properties of partly-fluorinated polymers

Fluorine-containing molecules are known to have low surface energy, and to partition to the interfaces in heterogeneous films. In paper 2, the architecture and morphology of fluorinated copolymers of methyl methacrylate was found to be important for controlling the surface energy of the materials when formed into thin films. Copolymers were prepared with different architectures, namely statistical and block arrangements of the monomer units. The surface energies decreased with increasing incorporation of the fluoro-monomer, in a manner consistent with previous reports for similar copolymers, however the surface energies of the block copolymers were consistently lower than the statistical copolymers. This was interpreted as arising from conformational restriction of presentation of the fluoro-monomers to the surface in the statistical copolymers, and formation of phase-separated domains at the surface of the block copolymers. The morphology of the block copolymers was confirmed by SAXS measurements, which allowed calculation of a solubility parameter for the fluorinated segments. The results have implications for the design of more environmentally acceptable materials with ultra-low surface energies.

List of Publications and Significant Collaborations that resulted from your AOARD supported project:

a) papers published in peer-reviewed journals,

1. Yi Guo, David J.T. Hill, Andrew K. Whittaker, Kevin S. Jack, Hui Peng Terpolymerization of Styrenic Photoresist Polymers: Effect of RAFT Polymerization on the Compositional Heterogeneity, *Macromolecules* (2015), 48, 3438–3448.
2. Ao Chen, Idriss Blakey, Kevin S. Jack, Andrew K. Whittaker, Hui Peng, Control through monomer placement of surface properties and morphology of fluoromethacrylate copolymers, *Journal of Polymer Science Part A: Polymer Chemistry* (2015), 53, 2633-2641.
3. Mahbub Alam, Hui Peng, Kevin S. Jack, David J.T. Hill, Andrew K. Whittaker, Reactivity ratios and sequence distribution characterization by quantitative ^{13}C NMR for RAFT synthesis of styrene-acrylonitrile (SA) copolymers, *Journal of Polymer Science, Part A: Polymer Chemistry* (2016), accepted 9th Nov 2016.

b) papers published in non-peer-reviewed journals or in conference proceedings,

None.

c) conference presentations,

1. Mahbub Alam, Yi Guo, Hui Peng, Kevin S. Jack, David J.T. Hill, Andrew K. Whittaker, Synthesis of Gradient Copolymers and Their Use in Remediation of Line Edge Roughness, 35th Australasian Polymer Symposium, Gold Coast, July 2015.
2. Yi Guo, Hui Peng, David J. T. Hill, Kevin S. Jack and Andrew K. Whittaker, Terpolymerization of Styrenic Photoresist Polymers: Effect of RAFT Polymerization on the Compositional Heterogeneity, 35th Australasian Polymer Symposium, Gold Coast, July 2015.

d) manuscripts submitted but not yet published, and

None – several in preparation.

e) provide a list any interactions with industry or with Air Force Research Laboratory scientists or significant collaborations that resulted from this work.

None.

DD882: As a separate document, please complete and sign the inventions disclosure form.

Important Note: If the work has been adequately described in refereed publications, submit an abstract as described above but cite important findings to your above List of Publications, and if possible, attach any reprint(s) as an appendix. If a full report needs to be written, then submission of a final report that is very similar to a full length journal article will be sufficient in most cases.

This document may be as long or as short as needed to give a fair account of the work performed during the period of performance. There will be variations depending on the scope of the work. As such, there is no length or formatting constraints for the final report. Keep in mind the amount of funding you received relative to the amount of effort you put into the report. For example, do not submit a \$300k report for \$50k worth of funding; likewise, do not submit a \$50k report for \$300k worth of funding. Include as many charts and figures as required to explain the work.